

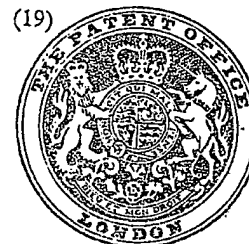
# PATENT SPECIFICATION

(11) 1331819

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## NO DRAWINGS

- (21) Application No. 20577/71 (22) Filed 19 April 1971  
(31) Convention Application No. 7250 (32) Filed 30 Jan. 1970 in  
(33) United States of America (US)  
(44) Complete Specification published 26 Sept. 1973  
(51) International Classification C08F 19/00  
(52) Index at acceptance



C3P 10D1A 10D2A 10D8 10K10 10K11 10K8 10P1D  
10P3 10P6A 10T2D 10T2X 11D2A1B 11D8 11K10  
11K4 11K6 11K7 11K8 11P1D 11P3 11P6A 11T2D  
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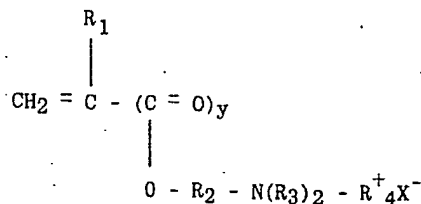
- (72) Inventors EUGENE SIGUND BARABAS and  
MARVIN MICHAEL FEIN

## (54) IMPROVEMENTS IN OR RELATING TO QUATERNIZED COPOLYMERS

### ERRATA

SPECIFICATION NO 1331819

Page 2, line 6 and Page 4, line 48, for existing formula read



THE PATENT OFFICE  
8 April 1974

R 74645/8

maleic anhydride, polyvinyl acetate—crotonic  
acid co- and terpolymers, half esters of ethylene—maleic anhydride as well as various  
25 others. With the exception of vinyl pyrrolidone homopolymers, all of the above conventionally employed synthetic polymers and resins used in hair sprays, wave set lotions, and hair  
30 conditioners give stiff hair-dos, thereby causing an unnatural look. In addition, such synthetic polymers or resins sometimes result in excessive flaking or excessive fly-away, thereby making preparations containing same unsatisfactory from a commercial standpoint.  
35

Although polyvinyl pyrrolidone homopolymers provide a more natural look in that they

of flaking and stiffening associated with previously employed polymer materials. 60

The polymers of the present invention are soluble in both water and alcohol and can be prepared in various molecular weights. The high molecular weight quaternized polymers act as their own thickeners in aqueous or alcoholic solutions, with the aqueous or alcoholic solutions of the quaternized polymers displaying a slippery feel and an ease of application to the hair. 65 70

The present invention accordingly provides a quaternized polymer having a structure derived from:

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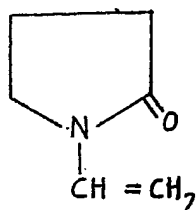
- (72) Inventors EUGENE SIGUND BARABAS and  
 MARVIN MICHAEL FEIN

## (54) IMPROVEMENTS IN OR RELATING TO QUATERNIZED COPOLYMERS

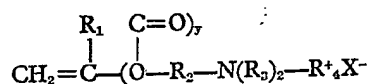
- (71) We, GAF CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, having its main office at 140 West 51st Street City, County and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to novel synthetic polymers which are copolymers or terpolymers, such synthetic polymers providing greater adhesion, greater holding power, and less flaking than conventional synthetic polymers used in hair preparations.
- At the present time the principal synthetic polymers or resins employed in hair sprays, wave set lotions, and hair conditioners include polyvinyl pyrrolidone homopolymers and copolymers, half esters of polyvinyl ethers—maleic anhydride, polyvinyl acetate—crotonic acid co- and terpolymers, half esters of ethylene—maleic anhydride as well as various others. With the exception of vinyl pyrrolidone homopolymers, all of the above conventionally employed synthetic polymers and resins used in hair sprays, wave set lotions, and hair conditioners give stiff hair-dos, thereby causing an unnatural look. In addition, such synthetic polymers or resins sometimes result in excessive flaking or excessive fly-away, thereby making preparations containing same unsatisfactory from a commercial standpoint.
- Although polyvinyl pyrrolidone homopolymers provide a more natural look in that they
- are free from some of the disadvantages of other commercially available products, the use of these homopolymers does not provide satisfactory holding of the hair at high humidity levels. This disadvantage of the use of polyvinyl pyrrolidone homopolymers in hair spray, wave set lotions and hair conditioner compositions has created the desire and necessity for the development of further synthetic polymers and resins substantially free from all of the above mentioned disadvantages. This development has now been accomplished with the present invention.
- A new type of polymer or resin has now been discovered which is useful in hair setting compositions including aerosol hair sprays, hair conditioners and hair setting lotions. These new quaternized derivatives of N-vinyl pyrrolidone polymers are particularly useful in hair setting compositions and provide excellent holding power and contribute to excellent body substantially without the disadvantages of flaking and stiffening associated with previously employed polymer materials.
- The polymers of the present invention are soluble in both water and alcohol and can be prepared in various molecular weights. The high molecular weight quaternized polymers act as their own thickeners in aqueous or alcoholic solutions, with the aqueous or alcoholic solutions of the quaternized polymers displaying a slippery feel and an ease of application to the hair.
- The present invention accordingly provides a quaternized polymer having a structure derived from:

SEE ERRATA SLIP ATTACHED

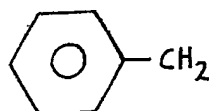
(A) 20—99 mole % of N-vinyl pyrrolidone of the formula



(B) 1—80 mole % of a compound having the general formula



wherein  $\gamma$  is 0 or 1;  $\text{R}_1$  is H or  $\text{CH}_3$ ;  $\text{R}_2$  is  $\text{C}_k\text{H}_{2k}$  where  $k=2$  to 18;  $\text{R}_3$  is  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  or  $t$ -butyl;  $\text{R}_4$  is  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  or



and X is Cl, Br, I,  $\text{HSO}_4$  or  $\text{CH}_3\text{SO}_3$ ; and

(C) 0—50 mole % of a vinyl or vinylidene monomer copolymerisable with N-vinyl pyrrolidone other than monomer (B).

For example, the quaternized polymer may have in accordance with this invention a structure derived from

(A) 40—90 mole % of the said N-vinyl pyrrolidone; and

(B) 5—40 mole % of a di-lower alkyl-aminoalkyl acrylate or methacrylate, and optionally up to 50 mol % of Component (C) as previously defined.

In this Specification "lower alkyl" means methyl, ethyl or  $t$ -butyl.

These quaternized polymers may be prepared by the copolymerization of N-vinyl pyrrolidone and di-lower alkylamine alkyl acrylate or methacrylate or a vinyl ether derivative, and optionally a further copolymerizable vinyl or vinylidene monomer (C) as defined above. Based upon 100 mole %, the vinyl pyrrolidone units (A) are present in an amount of 20—99%, the units (B) constitute from 1 to 80%, and the units (C) constitute from 0 to 50%.

Exemplary di-lower alkylamino alkyl-acrylates or methacrylates or vinyl ethers suitably employed in the production of the quaternized polymers of the present invention include:

dimethylaminoethyl acrylate  
dimethylaminoethyl methacrylate  
dimethylaminobutyl acrylate  
dimethylaminobutyl methacrylate  
dimethylaminoamyl methacrylate  
diethylaminoamyl methacrylate  
dimethylaminohexyl acrylate  
diethylaminohexyl methacrylate  
dimethylaminoethyl acrylate  
dimethylaminoethyl methacrylate  
diethylaminoethyl acrylate  
diethylaminoethyl methacrylate  
dimethylaminodecyl methacrylate  
dimethylaminododecyl methacrylate  
diethylaminolauryl acrylate  
diethylaminolauryl methacrylate  
dimethylaminostearyl acrylate  
dimethylaminostearyl methacrylate  
diethylaminostearyl acrylate  
diethylaminostearyl methacrylate  
di- $t$ -butylaminoethyl methacrylate  
di- $t$ -butylaminoethyl acrylate  
dimethylaminoethyl vinyl ether

The optional vinyl or vinylidene monomers Component (C) include any conventional vinyl or vinylidene monomer copolymerizable with N-vinyl pyrrolidone other than those of Component (B). Thus, for example, suitable conventional vinyl and vinylidene monomers include the alkyl vinyl ethers, e.g., methyl vinyl ether, ether vinyl ether, octyl vinyl ether; acrylic and methacrylic acid and esters thereof, e.g., methyl acrylate, methyl methacrylate; vinyl aromatic monomers, e.g., styrene,  $\alpha$ -methyl styrene; vinyl acetate; vinylidene chloride; acrylonitrile and substituted derivatives thereof; methacrylonitrile and substituted derivatives thereof; acrylamide and methacrylamide and N-substituted derivatives thereof; vinyl chloride, crotonic acid and esters thereof.

The polymers of the present invention are conveniently prepared by subjecting a solution of vinyl pyrrolidone (A) and the monomer (B), with or without an optical copolymerizable vinyl or vinylidene monomer (C), to conditions conducive to vinyl polymerization through the double bond and quaternizing the resultant copolymer. Thus, for example, polymerization may suitably be initiated by the action of free radicals, the polymerization proceeding exothermically once initiated. Suitable free radical catalysts conveniently employed and suitably utilized in accordance with the production of the polymers of the present invention include organic and inorganic peroxides, e.g., hydrogen peroxide, di- $t$ -butyl peroxide, aliphatic azo compounds, e.g., azobisisobutyronitrile as well as other free radical-forming catalysts well known in the polymerization art.

The polymerization is preferably carried out in solution at temperature varying from about 50°C to 100°C or more; however, to avoid

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runaway conditions and to obtain a copolymer of a desirable molecular weight it is sometimes preferred to carry out the polymerization at a temperature of from about 75 to about 85°C. The polymerization reaction is preferably carried out in the absence of free oxygen, conveniently under a blanket of a gas inert to the polymerization, such as, nitrogen, argon or the like, at atmospheric pressure.

In order to obtain the polymers of the present invention after completion of the polymerization reaction the polymer is submitted to a treatment conducive to quaternization of the tertiary amino group, utilizing a conventional quaternizing agent. Suitable quaternizing agents include, dialkyl, sulphates, e.g., dimethyl sulphate, diethyl sulphate; alkyl sulphonic acids, e.g., methyl sulphonic acid, ethyl sulphonic acid; benzyl halides, e.g., benzyl chloride benzyl bromide, benzyl iodide; alkyl halides, as well as other conventional quaternizing agents.

The polymers of the present invention generally have a Fikentscher K value within the range of 19 to 150 and, more particularly, within the range of 35 to 110 which corresponds approximately to a molecular weight within a range of 15,000 to 1,000,000, more particularly, within a range of 50,000 to 500,000. The polymers are eminently useful as hair spray resins in that they form clear, flexible and easily removable films from both aqueous and alcoholic solutions.

Generally, the polymers of the invention are produced including polymerization and quaternization in a period of a few hours, generally, within about ten hours.

The preparation of the polymers of the present invention will now be illustrated by the following specific examples, wherein parts and percentages are by weight.

#### EXAMPLE 1

A copolymer illustrative of the present invention was produced utilizing polymerization apparatus comprising a 5 litre kettle equipped with mechanical stirrer, reflux condenser, thermometer, and gas inlet tube. Some 1,225 parts of ethanol as a solvent were charged into the kettle and 800 parts of N-vinyl pyrrolidone and 200 parts of dimethylaminoethyl methacrylate were added and agitation was started. To the system was added one part of azobisisobutyronitrile and the system was purged thoroughly with nitrogen. The temperature of the system was raised to gentle reflux at about 85°C.

The polymerization reaction was promoted with further additions of catalyst (one part each) until the amount of residual monomer was below 0.6%. The system was thereafter cooled to 25°C and the speed of the agitation was increased.

In order to provide the quaternized deriva-

tive of the copolymer, 98.3 parts of diethyl sulphate were added from a dropping funnel over a period of thirty minutes. When the slightly exothermic reaction of quaternization was completed, the mixture was agitated for an additional period of thirty minutes. An analysis of the product produced indicated that the same contained 49.19% solids with the residual monomer content being 0.57%. The K value of the copolymer was 74.8, the same having a relative viscosity as measured as a 1% solution in ethanol of 2.837, and an intrinsic viscosity as measured in a 1% solution of ethanol 1.25 and a Brookfield viscosity of 26,000 cps.

#### EXAMPLE 2

Example 1 was repeated except that the dimethylaminoethyl methacrylate was replaced with substantially equivalent amounts of the following monomers:

- (a) dimethylaminomethyl acrylate
- (b) dimethylaminobutyl acrylate
- (c) diethylaminooctyl acrylate
- (d) diethylaminolauryl methacrylate
- (e) diethylaminostearyl methacrylate

The polymerizations were conducted in the same manner as in Example 1, and the corresponding copolymers were produced.

#### EXAMPLE 3

Example 1 was repeated except that the comonomers were employed in the following amounts:

- (f) 800 parts of N-vinyl pyrrolidone—100 parts dimethylaminoethyl methacrylate
- (g) 800 parts N-vinyl pyrrolidone—300 parts dimethylaminoethyl acrylate
- (h) 800 parts N-vinyl pyrrolidone—500 parts dimethylaminoethyl acrylate
- (i) 800 parts N-vinyl pyrrolidone—600 parts dimethylaminoethyl acrylate

The polymerization was carried out as in Example 1. The corresponding copolymers were produced, the ratio of the monomers dictating the ratio of the monomeric functions in the copolymer product.

#### EXAMPLE 4

Example 1 was repeated except that in addition to the dimethylaminoethyl methacrylate and N-vinyl pyrrolidone the following copolymerizable vinyl monomers were also utilized:

- (j) methyl vinyl ether—100 parts
- (k) octyl vinyl ether—200 parts
- (l) methacrylic acid—150 parts
- (m) methyl methacrylate—300 parts
- (n) styrene—200 parts
- (o) vinyl acetate—100 parts
- (p) vinylidene chloride 100 parts
- vinyl chloride—100 parts
- (q) methacrylonitrile—300 parts

The terpolymers so produced by following the polymerization techniques of Example 1 all had molecular weights within the range of 15,000 to 1,000,000. Each of the terpolymers was found to be eminently useful in hair spray compositions, forming clear, flexible, and easily removable films from both alcoholic solutions and aqueous systems.

#### EXAMPLE 5

Example 1 was repeated except that the following quaternizing agents were employed in lieu of diethyl sulphate:

- (r) dimethyl sulphate
- (s) ethyl sulphonic acid
- (t) benzyl chloride
- (u) benzyl bromide
- (v) benzyl iodide

Each of the copolymers so produced by the procedure of Example 1 was found to be eminently useful as a hair spray resin.

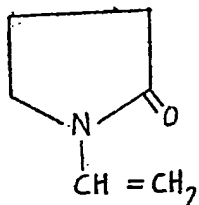
In addition to their utility as hair setting resins, the quaternized polymers of the invention are eminently suitable as textile treating agents for both woven and non-woven products when applied either by padding or by coating. They are capable of functioning as a size for the textile material either on a finished fabric or on the yarns or fibers used for weaving or otherwise fabricating the fabric, as a mordant for the finishes, as a dye receptor, as a non-toxic biocide or as a component of adhesives for lamination.

In addition such quaternized polymers have other applications as antistats, hand modifiers, deodorants and mildew preventers. In all these applications the use of the quaternized polymer of the invention leads to significant advantages in simplicity of application as well as durability of treatment.

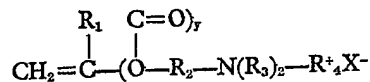
#### WHAT WE CLAIM IS:—

1. A quaternized polymer having a structure derived from:

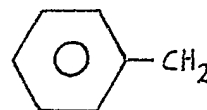
(A) 20—99 mole % of N-vinyl pyrrolidone of the formula



(B) 1—80 mole % of a compound having the general formula



wherein  $y$  is 0 or 1;  $\text{R}_1$  is H or  $\text{CH}_3$ ;  $\text{R}_2$  is  $\text{C}_k\text{H}_{2k}$  where  $k=2$  to 18;  $\text{R}_3$  is  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  or  $t$ -butyl;  $\text{R}_4$  is  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  or



and  $\text{X}$  is Cl, Br, I,  $\text{HSO}_4$  or  $\text{CH}_3\text{SO}_3$ ; and

(C) 0—50 mole % of a vinyl or vinylidene monomer copolymerisable with N-vinyl pyrrolidone other than monomer (B).

2. A quaternized polymer according to Claim 1, having a structure derived from

(A) 40—90 mole % of the said N-vinyl pyrrolidone; and

(B) 5—40 mole % of a di-lower alkyl-aminoalkyl acrylate or methacrylate, and optionally up to 50 mole % of Component (C) as defined in Claim 1.

3. The quaternized polymer according to Claim 1 or Claim 2, wherein the vinyl or vinylidene monomer (C) is selected from alkyl vinyl ethers, acrylic and methacrylic acids and esters thereof, vinyl aromatic compounds, vinyl acetate, vinylidene chlorides, vinyl chloride, acrylonitrile and derivatives thereof, methacrylonitrile and derivatives thereof, acrylamide and methacrylamide and N-substituted derivatives thereof, and crotonic acid and esters thereof.

4. The quaternized polymer according to any preceding claim, wherein component (B) is dimethylaminoethyl methacrylate.

5. A quaternized copolymer of vinyl pyrrolidone and dimethylaminoethyl methacrylate in accordance with Claim 1.

6. A quaternized polymer according to Claim 1 substantially as herein described and exemplified.

7. A method of producing a quaternized polymer defined in Claim 1 substantially as herein described and exemplified.

8. A quaternized polymer when obtained by the method claimed in Claim 7.

MEWBURN ELLIS & CO.,  
Chartered Patent Agents,  
70—72, Chancery Lane,  
London, WC2A 1AD,  
Agents for the Applicants.